The University of Chicago

I. The Conductivity of Alkaline Earth Formates in Anhydrous Formic Acid.

II. The Manufacture of Potassium Manganate.

A DISSERTATION

SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE SCHOOL OF SCIENCE IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY

R. D. MULLINIX

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I. THE CONDUCTIVITY OF ALKALINE EARTH FORMATES IN ANHYDROUS FORMIC ACID.

In previous work[1] on the behavior of the alkali metal formates dissolved in (anhydrous) formic acid, it was shown that when the degree of ionization is calculated from the conductivity uncorrected for viscosity, these very highly dissociated salts obey the law of chemical equilibrium up to relatively high concentrations. It was therefore considered important to investigate also some of the formates of bivalent metals, especially as there lay in this direction a possibility that light might be shed on the problem of the existence of intermediate ions in highly ionized salts. At the suggestion of Professor Schlesinger I chose for this purpose the formates of the alkaline earth metals.

The method and apparatus for preparing the formic acid and for making the conductivity measurements are described in a paper of this series by Schlesinger and Reed.[2] Calcium formate was prepared from a Kahlbaum sample by recrystallization until no further change in the conductivity resulted. The strontium salt was prepared by dissolving the carbonate in an aqueous solution of formic acid and evaporating the resulting solution, recrystallizing the resulting salt and drying it at a sufficiently high temperature to drive out the water. While all of the salts were analyzed and found pure within the limits of the ordinary analytical error, we used as criterion of their purity the fact that further recrystallizations produced no change in the conductivity of the salts when made up to a definite concentration in formic acid solutions.

In Tables I and II are given the experimental results found for calcium and strontium formate solutions, respectively. In the first column of each table is given the concentration c expressed in gram equivalents per liter, in the second column the specific conductivity χ in reciprocal ohms, in the third column the specific conductivity in reciprocal ohms

[1] *J. Am. Chem. Soc.*, **36**, 1599 (1914); **38**, 271 (1916).

[2] To be published in the near future.

corrected for the conductivity of the acid used as a solvent[1] in the fourth

TABLE I.

Conductivity of Solutions of Calcium Formate in Anhydrous Formic Acid at 25°.

$C.$	$\chi.$	$\chi a.$	$100\lambda a.$	$\lambda a.$	$a.$	$k.$
0.0000	.....	.....	1.8190	54.98	..	...
0.0415	0.0022252	0.0021622	1.9195	52.10	..	...
0.0646	0.0032420	0.0031808	2.0313	49.23	..	...
0.0784	0.0038153	0.0037541	2.0874	47.91	..	...
0.0951	0.0044780	0.0044150	2.1547	46.41	0.844	(0.435)
0.0969	0.0045564	0.0044830	2.1621	46.25	0.8413	(0.432)
0.1175	0.0053324	0.0052693	2.2310	44.82	0.8153	0.423
0.1461	0.0063716	0.0063085	2.3154	43.19	0.7856	0.421
0.1545	0.0066671	0.0066041	2.3395	42.74	0.7775	0.420
0.1650	0.0070468	0.0069834	2.3648	42.29	0.7692	0.423
0.1874	0.0077918	0.0077288	2.4248	41.24	0.7502	0.422
0.2043	0.0083288	0.0082655	2.4685	40.51	0.7369	0.422
0.2166	0.0087250	0.0086638	2.4994	40.01	0.7277	0.421
0.2498	0.009752	0.009687	2.5787	38.78	0.7054	0.422
0.2808	0.0106605	0.0105993	2.6491	37.75	0.6866	0.422
0.2979	0.0111495	0.0110885	2.6865	37.22	0.6771	0.423
0.3111	0.011508	0.011447	2.7176	36.80	0.6693	0.422
0.3202	0.011762	0.011700	2.7367	36.54	0.6647	0.422
0.3533	0.012641	0.012578	2.8087	35.60	0.6476	0.421
0.3778	0.013260	0.013197	2.8625	34.93	0.6355	(0.419)
0.3899	0.013563	0.013500	2.8878	34.63	0.6299	(0.418)
0.4362	0.014690	0.014627	2.9823	33.53	0.6099	(0.416)
0.4527	0.015065	0.015002	3.0178	33.14	0.6028	(0.414)
0.4925	0.015932	0.015869	3.1037	32.20	0.5861	(0.409)

TABLE II

Conductivity of Solution of Strontium Formate in Anhydrous Formic Acid at 25°.

$C.$	$\chi.$	$\chi a.$	$100/\lambda a.$	$\lambda a.$	$a.$	$k.$
0.0000	....	....	1.7582	56.876	..	...
0.0360	0.002039	0.001978	1.8206	54.928	0.9657	(0.979)
0.0476	0.002610	0.002549	1.8666	53.574	0.9419	(0.727)
0.0672	0.003525	0.003467	1.9404	51.536	0.9061	(0.587)
0.0964	0.004784	0.004724	2.0415	48.983	0.8612	(0.515)
0.1117	0.005426	0.005365	2.0825	48.020	0.8443	(0.511)
0.1380	0.006475	0.006413	2.1512	46.486	0.8173	0.505
0.1604	0.007343	0.007282	2.2032	45.389	0.7980	0.506
0.1784	0.008016	0.007956	2.2430	44.583	0.7839	0.507
0.1868	0.008312	0.008251	2.2634	44.181	0.7768	0.505
0.2358	0.010019	0.009959	2.3673	42.243	0.7427	0.505
0.2565	0.010725	0.010664	2.4054	41.573	0.7309	0.509
0.2718	0.011207	0.011146	2.4390	41.001	0.7209	0.506
0.3001	0.012106	0.012045	2.4911	40.143	0.7058	0.508
0.3149	0.012549	0.012488	2.5213	39.663	0.6973	0.506
0.3443	0.013418	0.013357	2.5777	38.796	0.6821	(0.504)
0.3859	0.014578	0.014517	2.6579	37.637	0.6617	(0.499)

[1] The specific conductivity of the acid used for these experiments averaged about 6.3×10^{-5}.

column the corrected equivalent conductivity λ_a, in the fifth column 100 divided by the equivalent conductivity, in the sixth column a, which is a calculated value which corresponds to what would be the degree of ionization for the case of the uni-univalent salts and which we obtained in the manner described below, and in the sixth column K, a constant over a certain range of the concentrations investigated, calculated as explained later.

For the purpose of interpreting our experimental data, we followed the method used in the earlier papers. It is possible to cast the mass law for uni-bivalent salts into a form in which suitable plotting would result in a straight line if the mass law were obeyed. Our data plotted in this way did not give a straight line. It occurred to us that the cause of this lack of agreement might be ionization into an intermediate ion—in the case of the calcium formate, for example into $CaOCHO^+$ and $OCHO^-$. We therefore plotted the values of $100/\lambda$ against $c\lambda$, which according to the equation $1/\lambda = 1/\lambda_0 + (1/K\lambda_0^2)c\lambda$ gives a straight line in the cases of uni-univalent salts which obey the mass law. These plots are shown in Fig. 1. For the purpose of comparison, the corresponding curve for sodium formate, taken from the work of Schlesinger and Reed,[1] has been added.

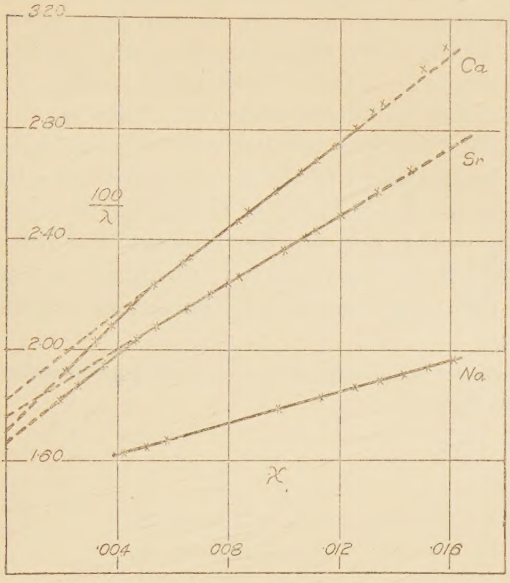

Fig. 1.

It will be seen that the curves for the alkaline earth formates differ in some respects from those obtained for the uni-univalent salts. The latter are straight lines, without a break from the lowest concentrations which have thus far been accessible to reliable measurement to a concentration varying from 0.28 to above 0.45 normal in the different salts. At higher concentrations a deviation of a nature to be expected[2] has been observed for all of the uni-univalent salts investigated. The curves for the alkaline earth formates on the other hand consist of three sections. The portion of the curve representing the lower concentrations consists, so far as the

[1] *Loc. cit.*

[2] Schlesinger and Martin, *J. Am. Chem. Soc.*, **36**, 1599 (1914).

data now available indicate, of two straight lines which intersect at a concentration in the neighborhood of 0.1 equivalent. From this point of intersection upward the curves for these salts are in all respects like those for the alkali metal formates.[1] It is therefore clear that two sets of values can be found for the terms λ_o and K in the equation given on a previous page. The values calculated for the tables are those referring to the points on the middle portion of each of the curves.

We are as yet unable to give a satisfactory explanation of the behavior of these alkaline earth formates. It is quite likely that these salts ionize into a metal formate ion which in the more dilute solutions is somewhat decomposed into the simple metal ion and that this second ionization becomes sufficiently great at the concentration where the two lines intersect to affect the conductivity appreciably. It is not clear why, if this interpretation is correct, there should be a sharp break at this point. It was our intention to investigate these questions further by studies on the solubilities of these formates in the presence of salts with common ions and also to make possible the measurement of the conductivities at still lower concentrations by reducing the conductivity of the solvent by new means which have been partially worked out, but this intention was frustrated by the necessity of taking up the work which is described in the second part of this dissertation and which was of more immediate importance in connection with the war.

[1] In the reproduction of the curve for sodium formate, the upper portion which deviates from the straight line is not shown.

II. THE MANUFACTURE OF POTASSIUM PERMANGANATE

Among the important chemicals which in the past have been imported at so low a price that American manufacturers had not, up to the time of the European war, undertaken its production to any large extent is potassium permanganate. The obvious need for the product and its extreme scarcity have, however, made its manufacture in this country a necessity, and a number of plants are now engaged in producing it. Some of them encountered certain difficulties when they began continuous operation and Professor Schlesinger was asked by the Bureau of Mines to investigate the matter. At his suggestion I therefore undertook the work described below.

There are several methods for manufacturing the permanganate; the most widely used is apparently the one in which potassium manganate is first prepared as an intermediary product by heating a mixture of potassium hydroxide and manganese dioxide in a current of air. The resulting mix is then extracted with water or a dilute solution of caustic potash and the solution of manganate thus obtained is converted into a solution of the permanganate. The methods employed for this latter step need not be discussed here as the research now to be reported deals only with the first step. It is necessary, however, to point out that in this second step a large proportion of the caustic combined in the first is again liberated either in a form in which it can be directly utilized or in which it can be used after suitable treatment, depending upon the process used for the second step. Furthermore, owing in part to the spontaneous decomposition of manganate and permanganate solutions, in part to manganese dioxide precipitated out in the second step and in part to the fact that the first step never results in complete interaction of the components, there is always a relatively large amount of manganese dioxide left over from each treatment. It is therefore self-evident that economical working of the process not only requires as high a yield as possible of the manganate in the first step, but that it

is also necessary that the reutilization of the residual and recovered manganese dioxide and potassium hydroxide must be highly successful. Difficulties have apparently been encountered in both of these phases of the process and we have therefore made a study of the factors which influence their successful carrying out.

The conversion of manganese dioxide into potassium manganate by heating it in a current of air with potassium hydroxide has been extensively investigated. The most recent and apparently the most thorough of these investigations are those of Askenasy and Klonowski[1] and of Sackur[2] and his associates. The researches of the two groups of investigators do not lead them to the same conclusion. While the first named seem to hold to the opinion that the reaction follows the course usually found in the text books, represented by the equation

$$4KOH + 2MnO_2 + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O,$$

Sackur concludes that potassium manganate is never formed in this way, but that the product obtained in the reaction is a "mangani-manganate" which can be represented by the formula, $2K_2MnO_3,3K_2MnO_4,3K_2O$. In this conclusion he is corroborated by the work of Auger[3] who obtained a compound of similar composition by heating potassium permanganate with excess of potassium hydroxide. If Sackur's conclusion is correct it is clear that the highest yield that could be obtained in the reaction in terms of the amount of manganese dioxide oxidized to the manganate stage could be only 60 per cent, since the remaining 40 per cent must always remain as manganite. In support of this consequence of his theory of the course of the reaction Sackur cites his own experiments which show a maximum yield of between 55 and 66 per cent, the results of Askenasy and Klonowski who obtained similar yields, and the statements, made personally to Sackur by German manufacturers, that a yield of 60 per cent was the maximum attained in practice.[4] When we first undertook this

[1] *Z. Elektrochem.*, **16** (1910), 104, 170.

[2] *Ber.*, **43** (1910), 381, 448; **44** (1911), 777; *Z. Elektrochem.*, **16** (1910), 649; **18** (1910), 718; *Z. anorg. Chem.*, **73** (1912), 101.

[3] *Compt. rend.*, **151**, 69.

[4] It will be noted that the highest yields obtained by Sackur are a little higher than permitted by his theory. Sackur gives an explanation of this which the work herein reported shows to be incorrect. Askenasy in one experiment obtained very much higher results than Sackur. The experiment, however, has not been cited in refutation of Sackur's criticism of Askenasy and it is, therefore, likely that the result was never confirmed.

investigation the manufacturers with whom we were coöperating were not obtaining yields as high as those demanded by Sackur's theory and we, therefore, attempted to determine the best conditions for duplicating his results.

In our experiments we decided to follow the procedure of Askenasy and Klonowski.[1] This procedure consists, briefly stated, in mixing the finely ground ore with a concentrated solution of caustic potash, drying the mix in a current of air to such a consistency that when cool it can be well powdered and will no longer become soft on raising it to the higher temperatures to which it is next exposed, and finally heating this powdered material in a current of air in an apparatus in which the mix can be continually ground while being heated. This apparatus consisted of a rotating drum, fitted with iron ribs parallel with the axle and with openings for removing material for analysis. The drum was rotated in an iron housing and was heated by gas. The axle was hollow and broken in the middle of the drum. Through one end of the hollow axle preheated air was introduced and into the other end a thermocouple was loosely fitted. The charge, prepared as above, was placed in the drum and with it a fairly large number of $^3/_4$ in. steel balls. As the drum rotated slowly (20 r. p. m.) the balls were lifted by the ribs in the sides of the drum and dropped back on the material, thus pulverizing the latter thoroughly throughout the process. That this continuous pulverization, which is recommended by the authors named above, considerably improves the yield was corroborated by our own results, which need not be recounted here. In only two particulars did we depart from the method of Askenasy and Klonowski. In the first place in making the mix we used ore and alkali in the proportions described below while they used mixtures containing approximately equal parts by weight. In the second place we used a somewhat lower temperature, keeping our mixes in the rotators at about 450° C. In one minor matter we also departed from the older investigation referred to. The preliminary drying was carried out in an electrically heated oven instead of over a free flame, but this was merely a matter of convenience in regulating the temperature at this stage and in avoiding too great a contamination with carbon dioxide,

[1] *Loc. cit.*, p. 175.

which is likely to occur when the heating is carried out over the free flame. The heat was so regulated in this part of the process that when the mix was completely dry its temperature remained in the neighborhood of 300° C.

The preliminary heating, while it results in the absorption of some oxygen and in some experiments to quite a large amount, is in general carried out merely to prepare the material for the treatment in the rotary kilns in which the chief absorption usually takes place. The mass was usually analyzed after the preliminary heating was completed and, after it was placed in the kilns, analysis was repeated every few hours until oxygen absorption seemed to cease. This could be done without cooling off the whole mass because material could be withdrawn from the cylinders through the openings mentioned. The method of analysis was that employed by Askenasy and Klonowski.

Before proceeding to the discussion of the final results of this part of the investigation one important detail must be taken up. In one of our earlier experiments a mix was heated in the rotary kiln, as described, first in an atmosphere of dry air and then in oxygen. The potassium manganate content in air rose to 54.6 per cent, which is about 60 per cent of the yield possible according to the equation given above. Further heating in air caused a slight lowering of the yield. In oxygen the content of manganate rose to 63 per cent, at which point absorption of oxygen came to an end. The mass was then treated with enough water so that the mixture could be well stirred. It was then dried as described above and reheated in oxygen in the kilns at 450°. The manganate content now rose to 77.9 per cent and a repetition of this procedure finally raised it to 81 per cent, representing a yield of 92 per cent of the theoretical on the assumption that manganate and not mangani-manganate is the product obtained. Frequent repetitions of analogous experiments showed that it was the moistening with water which raised the final yields, as merely by this treatment and without the use of oxygen we have been able to reproduce these and higher yields. Two questions were raised by this result. In the first place it would seem as if manganate is not as sensitive to moisture as usually stated. To bear this out the following may be cited. Steam was passed over a product containing 78.6 per cent of potassium man-

ganate for 20 min. while the mass was kept at 450°. At the end of this time the manganate content had fallen only to 76.8 per cent. It is clear, therefore, that under the conditions prevailing, moisture cannot be very harmful in the process. It may, in fact, be necessary to obtain the highest yields. The latter point has been further investigated and discussed by Popoff.[1] For the purpose of this investigation it is sufficient to state that by the experimental procedure just described, the yields obtained by Sackur could readily be exceeded with the raw materials used in this work.

After we had in this way shown how good results could be obtained with these raw materials, we took up the question raised by the fact, reported to us by a manufacturer, that new caustic and new manganese dioxide may give very much higher yields than are obtained when the residual and recovered materials are mixed with the new. It is manifest that there can be only two possible causes for the deterioration—either impurities are introduced into the materials in the course of the process or the manganese dioxide must become changed into a less active modification. In order to clear up this point we proceeded, after we had determined what yields might be expected as has been described, to work with the recovered alkali and the residual dioxide. While a few experiments were carried on in which both were used, the yields obtained were so very low that we abandoned this line and attacked the question by working with new manganese dioxide ore and recovered alkali in one set of experiments and with residual manganese dioxide and new caustic in another set.

The first of these two sets of experiments was the one in which new ore and recovered caustic were used to make up the mixes. The caustic was furnished us in the form of a fairly concentrated solution. It was colored green by a small amount of unconverted manganate. After analysis[2] of the solution it was mixed with enough of the ore to produce a mix of the desired proportions. This was then treated exactly as has been described in the earlier portions of the paper.

[1] Dissertation, University of Chicago, 1919.

[2] Before analysis of the solutions, they were freed from manganate by reducing it to manganese dioxide by the addition of a drop or two of formaldehyde solution. After the manganese dioxide had been filtered off, the clear solution could be titrated for free alkali or carbonate by any of the customary methods. The use of formaldehyde, while not entirely free from objection, introduced no error large enough to be of importance for this work.

The mixes were made up to contain from 2.17 to 2.33 moles of potassium hydroxide to one mole of manganese dioxide—a proportion chosen because it conformed to that used by the manufacturer with whom we were coöperating and from whom we obtained all of the recovered or regenerated materials. When we substituted the recovered alkali for the new a very striking lowering of the yield resulted, for we were not able to obtain one better than about 27 to 30 per cent and repeated remoistening and treatment with oxygen even under a pressure of 40 lbs.[1] produced no improvement. There is, therefore, no doubt that these solutions contain some impurity which interferes with the success of the reaction. The foreign substances present in greatest amount were carbonate, chloride, manganate, silicate, and sodium. It was found that the first four named had no appreciable effect on the yield when they were separately added to new materials. Likewise, no other impurities removable by calcium hydroxide could have been responsible for the difficulty, since careful causticization of the liquor did not improve it.[2]

The case was found to be quite different when the effect of sodium was investigated. Analysis of the liquors furnished us showed in different samples that from 25 to 40 per cent of the alkali was in the form of sodium hydroxide. When mixes were made up from new material in which we used pure sodium hydroxide and pure potassium hydroxide in these same proportions the yields resulting were, respectively, 38 and 27 per cent. It was clear at once that here lies the source of the difficulty.[3]

Although we have shown in the preceding section of this paper one of the causes of the decrease in the efficiency of the process when recovered material is used, there is still the possibility that the recovered manganese dioxide also may not be as satisfactory as the new ore.

We therefore made another set of experiments in which we used recovered and residual manganese dioxide with new potassium hydroxide. The former was

[1] A series of experiments was conducted to determine the effect of oxygen under pressure (20 to 40 lbs.). So far as we have been able to determine up to the present such treatment merely hastens the oxidation but does not affect the final yield.

[2] The recovered alkali must of course be causticized from time to time since the carbonate is apparently quite inert at the temperatures best employed for the manufacture of manganate.

[3] For a more detailed discussion see S. Popoff's dissertation, *loc. cit.*

obtained from the same manufacturer who had furnished us with the recovered alkali described above. The ratio of alkali to manganese dioxide was again 2.28 moles of the former to one of the latter. When the old manganese dioxide, as we may call the material for brevity, was used just as it was received, it gave uniformly low yields—from 25 per cent to 35 per cent of the theoretical—while we should have obtained about 85 per cent. Since it is well known that manganese dioxide absorbs (or perhaps combines with) relatively large amounts of caustic alkalies, we suspected that the old dioxide might be contaminated with considerable sodium hydroxide. We therefore washed it very thoroughly with water and in some cases boiled it with dilute nitric acid. When the recovered and residual dioxide was fresh it responded very well to this treatment; material which had been kept for some time, and especially material which had dried out, was not much improved. These results point to the conclusion that it was the absorbed sodium hydroxide which was responsible for the deteriorating of the dioxide and which becomes more difficult to remove as the material dries out.

In conclusion I wish to thank Prof. Schlesinger whose advice and supervision were of great aid in the completion of this investigation and to acknowledge the coöperation of Mr. S. Popoff in the experimental work.